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A comparison of samples preparation strategies in the multi-elemental analysis of tea by spectrometric methods

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ABSTRACT

Tea made from *Camellia sinensis* plant is one of the most widely consumed beverages worldwide. It is recognized as a rich source of various elements, including those being essential to human health and also toxic that the plant may accidentally take up during the growth period and which can have adverse effects on the human well-being. Due to the habitual drinking of tea infusions, the determination of the mineral content in tea is of a great importance in order to control the quality and the safety of this product or to judge its nutritional value. In general, atomic and mass spectrometries are commonly used for the elemental analysis of tea leaves and commercial teas. Although these analytical techniques are useful in measurements of the total concentration of elements, they usually require samples to be properly pre-treated prior to spectrochemical measurements. Because the sample preparation of tea is the most critical step of the whole analytical chain, this review has been attempted to survey different preparation procedures of tea samples carried out before the element analysis. Common strategies aimed at decomposing samples through dry and wet digestions are described in details and compared in reference to their advantages and drawbacks. Recent, alternative methods of the sample treatment and the analysis by spectrometry techniques are also highlighted. The effect of the selection of certain sample preparation procedures on the reliability of analytical results and manners of the control and the assurance of their quality are also considered.

1. Introduction

Tea prepared from dried leaves of the *Camellia sinensis* plant is the most popular non-alcoholic beverage worldwide because of its aroma, taste, smell, variety of types and multiple positive health-promoting effects (Ashraf & Mian, 2008; Desideri, Meli, Roselli, & Feduzi, 2011; Ipeaiyeda & Dawodu, 2011; Salahinejad & Aflaki, 2010; Srividhya, Subramaniam, & Raj, 2011). Depending on the degree of the fermentation process, green (unfermented), black (fully fermented) and oolong (partially fermented) teas are the most popular and frequently consumed (Desideri et al., 2011; Malik, Szakova, Drabek, Balik, & Kokoska, 2008; McKenzie, Jurado, & De Pablos, 2010; Mehra & Baker, 2007; Shen & Chen, 2008). At present, a booming consumption of other teas, e.g., pu-erh (post-fermented) can be observed since it is noteworthy for medicinal purposes and recognized to has many beneficial health effects (Cao, Qiao, Zhang, & Chen, 2010; Lv, Lin, & Guo, 2012; McKenzie et al., 2010).

The chemical composition of tea leaves and made teas is complex, being in the majority (>90% (m/m)) a mixture of different organic compounds, including polyphenols, alkaloids, proteins, amino-acids, enzymes, aroma-forming substances, carbohydrates and vitamins (Kumar, Nair, Reddy, & Garg, 2005; Soylak, Tuzen, Souza, Korn, & Ferreira, 2007; Srividhya et al., 2011; Street, Drabek, Szakova, & Mladkova, 2006; Yemane, Chandravanshi, & Wondimu, 2008). Besides of these organicals, tea leaves and made teas are rich in different elements, counting major, minor and trace elements (see Table 1). The content of element is characteristic to tea types and mostly attributed to the specific way that these teas are manufactured as well as the geographical origin of tea plants referring to soil composition, climate, local environmental conditions and agricultural practices (Aksuner, Henden, Aker, Engin, & Satik, 2012; Ashraf & Mian, 2008; Chen, Yu, Xu, Chen, & Shi, 2009; Desideri et al., 2011; McKenzie et al., 2010; Mehra & Baker, 2007; Soylak et al., 2007; Street et al., 2006). Some elements, i.e., Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Se, V and Zn, are essential to the human health and therefore may contribute to a nutritional value of tea (Aksuner et al., 2012; Ashraf & Mian, 2008; Desideri et al., 2011; Ipeaiyeda & Dawodu, 2011; Malik et al., 2008; Nookabkaew, Rangkadilok, & Satayavivad, 2006; Salahinejad & Aflaki, 2010; Street et al., 2006; Yemane et al., 2008). Unfortunately, *Camellia sinensis* plant can tolerate and accumulate quite elevated quantities of Al and F (Fung, Carr, Poon, & Wong, 2009; Pehrsson, Pattterson, & Perry, 2001), and other unessential and undesirable elements (e.g., Pb, As, Cd, Hg) originated from atmospheric dusts, rainfalls or fertilizers used during stages of plant growth or from manufacturing processes when ready-made teas are produced (Aksuner et al., 2012; Cao et al., 2010; Chen, Xu, Yu, Chen, & Shi, 2010; Desideri et al., 2011; Han, Shi, Ma, & Ruan, 2005; Lv et al.,

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Table 1
Proximate elemental contents (in μg/g) of made teas (on the basis of results for black, green and oolong teas reported by Szymczycha-Madeja et al., 2012).

Elements							
Major		Minor		Trace			
Al	$(0.02–27.0) \times 10^3$	B	3.10–14.0	Ag	ND–0.05	Pb	ND–240
Ca	ND–4.60×10^4	Ba	0.57–63.0	As	ND–10.2	REEs	ND–4.22
K	$(0.63–2.99) \times 10^4$	Cr	ND–129	Be	ND	Sb	ND–0.08
Mg	0.09×10^3–3.40×10^4	Cu	0.03–602	Bi	ND–0.28	Se	ND–16.4
Mn	ND–1.50×10^4	Fe	0.03–1.30×10^4	Cd	ND–8.60	Sn	ND–0.81
Na	3.00–3.20×10^4	Mo	ND–571	Ce	0.51–0.59	Te	ND–0.16
P	$(1.35–5.79) \times 10^3$	Ni	ND–1.96×10^3	Co	ND–17.4	Tl	0.03–10.7
S	$(2.04–3.83) \times 10^3$	Rb	23.1–152	Cs	0.08–0.84	U	0.006
		Sr	0.16–72.4	Hg	ND–0.76	V	ND–29.0
		Ti	ND–263	In	ND–0.92	Y	0.36
		Zn	ND–1.12×10^3	Li	ND–16.0	Zr	ND–0.70

ND: Not detected.
REEs: rare earth elements.

2012; Malik et al., 2008; Nookabkaew et al., 2006; Qin & Chen, 2007; Seenivasan, Manikandan, Muraleedharan, & Selvasundaram, 2008; Shen & Chen, 2008). More detailed information about the content of elements in tea leaves, made teas and tea infusions can be found in three other mechanistic reviews (Karak & Bhagat, 2010; Szymczycha-Madeja, Welna, & Pohl, 2012; Welna, Szymczycha-Madeja, Stelmach, & Pohl, 2012).

Considering different properties of elements (essential or toxic) and significant contribution of tea to daily intakes of elements due to habitual drinking of tea infusions, it seems that the determination of total concentrations of elements in tea products is of a great importance (Salahinejad & Aflaki, 2010; Street et al., 2006). In addition, the analysis of tea according to the content of various elements, particularly of toxic metals, is indispensable to understand its nutritive properties and control the quality and the safety of tea products (Aksuner et al., 2012; Ashraf & Mian, 2008; Cao et al., 2010; Desideri et al., 2011; Han et al., 2005; Ipeaiyeda & Dawodu, 2011; Lv et al., 2012; Malik et al., 2008; Salahinejad & Aflaki, 2010; Shen & Chen, 2008; Srividhya et al., 2011; Street et al., 2006; Yemane et al., 2008).

Since the awareness and the concern about elements in tea are great, the present paper is devoted to basic principles of the elemental analysis of tea by atomic and mass spectrometry techniques and systematically surveys included sample preparation steps. Different preparation procedures of tea samples before spectrochemical measurements, reported in the published literature in past 10 years, are reviewed and compared.

2. Determination of elements in tea leaves and made teas by spectrometric methods

2.1. General rules

As can be seen from Table 2, the determination of total concentrations of various elements in samples of tea leaves and made teas are primarily performed using spectrochemical methods such as flame- and graphite furnace atomic absorption spectrometry (F- and GF-AAS), inductively coupled plasma optical emission spectrometry (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS). It seems that the two latter ICP-based techniques are the most effective in the multi-element analysis of tea samples. Hydride generation (HG) combined with spectrometric detectors, i.e., atomic fluorescence spectrometry (AFS), is preferred for measurements of hydride forming elements, e.g., As, Bi, Se, Te (Zhang, Fu, Fang, Feng, & Ke, 2011).

Atomic spectrometry techniques listed in Table 2 commonly required samples in the form of aqueous or acidic solutions (Dash, Manjusha, Thangavel, & Arunachalam, 2008). Therefore, solid tea leaves and manufactured teas samples have to be initially prepared

Table 2
Examples of recent applications of open-vessel and closed-vessel MW-assisted wet digestion procedures for the analysis of tea samples analysis.

Reagent (ratio, v/v)	Samples	Determined elements (detection)	Reference
Open-vessel wet digestion			
$HNO_3 + HClO_4$ (1 + 4)	Black, green, oolong, scented teas	Cu, Pb (GFAAS)	Qin and Chen (2007)
$HNO_3 + HClO_4$ (3 + 2)	Black tea	Al, As, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Zn (ICP-OES)	Salahinejad and Aflaki (2010)
$HNO_3 + HClO_4$ (5 + 1)	Tea leaves (green)	Ca, Cd, Co, Cu, Fe, K[a], Mg, Mn, Na[a], Pb, Zn (FAAS)	Yemane et al. (2008)
$HNO_3 + HClO_4$ (7 + 8)	Black, green, white teas	Cu, Fe, K[a], Mn, Na[a], Ni, Zn (FAAS)	Aksuner et al. (2012)
$HNO_3 + HClO_4$ (10 + 1)	Black tea	Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn (ICP-OES)	Ashraf and Mian (2008)
$HNO_3 + HClO_4$ (14 + 1)	Black, green, oolong teas	Ba, Bi, Cd, Ce, Co, Cr, Cs, Cu, Eu, Ga, La, Nb, Ni, Pb, Pr, Rb, Sr, Ti, Tl, Y (ICP-MS)	Pilgrim et al. (2010)
$HNO_3 + HClO_4$ (16 M + 12 M)	Tea leaves (green)	Al (FAAS) Ca, Cu, K, Mg, Zn (ICP-OES)	Li et al. (2007)
HNO_3 + HCl (2 + 1)	Black, green teas	Cu, Fe, Mn, Pb, Zn (ICP-OES)	Görür et al. (2011)
HNO_3 + HCl (3 + 1)	Black tea	Cd, Co, Cr, Cu, Mg, Ni, Pb, Zn (FAAS)	Narin et al. (2004)
HNO_3	5 different non-specified teas	Mn, Fe, Cu, Zn (FAAS)	Ipeaiyeda and Dawodu (2011)
HNO_3	Black, green teas	Ba, Ca, Ce, Cu, Fe, K, Mg, Mn, Na, Ni, P, Sr, Zn (ICP-OES) Ce, Co, Cr, La (ICP-MS)	Kara (2009)
HNO_3 $HNO_3 + HClO_4$ (8 + 0.5; 8 + 1) (if necessary)	Pu-erh tea and tea leaves	Al, As, Cd, Cu, Hg, Pb, Zn (ICP-MS)	Cao et al. (2010)
Closed-vessel MW-assisted wet digestion			
HNO_3	Black tea	Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Ln, K, Li, Mg, Mn, Na, Ni, P, Pb, S, Sr, Ti, V, Zn (ICP-OES)	Özcan et al. (2008)
HNO_3	Black, green, oolong teas	As, Cd, Co, Cr, Cu (ICP-OES)	Han et al. (2005)
HNO_3	Black, green, oolong teas	As, Cd, Co, Cr, Cu, Fe, Mg, Pb, Se, Zn (ICP-MS)	Shen and Chen (2008)
HNO_3	Pu-erh tea	As, Cd, Cr, Cu, Pb (ICP-OES)	Lv et al. (2012)
$HNO_3 + H_2O_2$ (3 + 1)	Non-specified tea products	Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb Se, Sb, Sr, V, Zn (ICP-MS)	Nookabkaew et al. (2006)
$HNO_3 + H_2O_2$ (3 + 1)	Black, green teas	Cu, Ni, Zn (FAAS)	Soylak et al. (2007)
$HNO_3 + H_2O_2$ (3 + 1)	Black, green, white teas	Cu, Fe, K[a], Mn, Na[a], Ni, Zn (FAAS)	Aksuner et al. (2012)
$HNO_3 + H_2O_2$ (6 + 1)	Black, green, oolong, pu-erh, white teas	Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, P, S, Sr, Zn (ICP-OES)	McKenzie et al. (2010)
HNO_3 + HCl (3 + 1)	Black tea	Cd, Co, Cr, Cu, Mg, Ni, Pb, Zn (FAAS)	Narin et al. (2004)
HNO_3 + HCl + HF (7.5 + 2.5 + 1)	Oolong tea	Ba, Ca, Fe, Pb, Zn (ICP-OES)	Mierzwa et al. (1998)
$HNO_3 + H_2O_2 + HClO_4$ + HF (3 + 0.4 + 0.2 + 0.2)	Tea leaves (green)	Rare earth elements (REEs) (ICP-MS)	Cao et al. (1998)

[a] An emission mode or a flame photometer was used.